A self-supporting graphene supported cobalt hydroxide for enhanced oxygen evolution catalysis

Libei Chen [a], Jianbing Zang [a], Xiaoxu Liu [a, b], Yan Zhang [a], Shaopei Jia [a], Pengfei Tian [a], Yanhui Wang [a, *]

[a] State Key Laboratory of Metastable Materials Science and Technology, School of Materials Science and Engineering, Yanshan University, Qinhuangdao, 066004, PR China
[b] Department of Physics, Hebei Normal University of Science and Technology, Qinhuangdao, 066004, PR China

ARTICLE INFO

ABSTRACT

A self-supporting graphene (SSG) was fabricated to act as a highly conductive catalyst support via electrochemical intercalation for a flexible graphite sheet (FGS) in 1 M KOH solution. Then cobalt hydroxide ($Co(OH)_2$) was deposited on the surface of SSG through a convenient microwave-polyol method. The resulting electrode ($Co(OH)_2$/SSG-FGS) exhibited remarkable catalytic performance for oxygen evolution reaction (OER) in alkaline solution, which was closely related with the unique structural advantage of the composite electrode. The self-supporting structure of $Co(OH)_2$/SSG-FGS possessed the current collector and provided conducting channels for $Co(OH)_2$ particles, enabling fast electron transfer from $Co(OH)_2$ active sites along SSG to the FGS current collector and enhancing the catalytic performance of $Co(OH)_2$/SSG-FGS for OER. Therefore, the $Co(OH)_2$/SSG-FGS just required an overpotential of 140 mV to achieving $10 \, mA \, cm^{-2}$ in 0.1 M KOH solution, which even surpassed the commercial RuO_2 catalyst. Additionally, the excellent stability of $Co(OH)_2$/SSG-FGS highlighted its efficiency and made it preferable as an efficient catalyst for OER.

© 2018 Elsevier Ltd. All rights reserved.

1. Introduction

The growing energy demand and serious environmental pollution are vital issues facing humanity, so it is highly advisable to research and develop efficient and clean energy conversion and storage technologies, for instance, fuel cells, metal-air batteries, and water electrolysers [1–5]. Oxygen evolution reaction (OER) is not just one of the most critical electrochemical processes, but the kinetic bottleneck for these energy technologies due to its sluggish kinetics [6,7]. Currently, precious metal oxides, such as IrO_2 and RuO_2, exhibit excellent catalytic performance for OER, but their high cost and scarcity hinder their wide application [8,9]. Accordingly, considerable efforts have been put into developing earth-abundant, efficient and durable precious metal-free OER catalysts.

Up to now, various cobalt-based materials, including cobalt hydroxide ($Co(OH)_2$) [10], cobalt oxyhydroxide (CoOOH) [11], cobalt oxide (Co_3O_4) [12–14] and other cobalt compounds [15–17] have been investigated and showed excellent electrocatalytic activity for OER. Whereas the intrinsically poor conductivity of cobalt compounds impedes their further commercial applications. One of the resultful approaches to improve the conductivity is combining cobalt compounds with carbon materials which possess high conductivity. Graphene, the two-dimensional one-atom-thick layer, holds great promise as supports for catalysts because of extraordinary conductivity, high specific surface area and excellent stability. However, graphene may reunite into graphite owing to the π-π stacking and Van der Waals interactions while preparing, drying and following processing, which will result in the decrease of surface area [18,19]. Adhering catalytic nanoparticles onto graphene sheets can inhibit the aggregation effect and simultaneously improve the catalytic activity [20]. But the original ultrahigh conductivity advantage will be significantly weakened. The reason is that the graphene sheets are separated by catalytic nanoparticles with the relatively poor conductivity, which is adverse to electron transport. Therefore, self-supporting 3D graphene structures, such as 3D porous graphene foam and 3D graphene aerogel have drawn worldwide attention [21–25]. Though 3D graphene structures possess large surface area and avoid graphene layers stacking, the

---

following electrode preparation still needs extra current collector and binders, which inevitably reduce the catalytic activity and stability of the electrode [26]. To address such challenges, many researchers devote themselves to exploiting new approaches to prepare 3D composite materials which include the current collector and avoid or reduce the aggregation of graphene layers stacking simultaneously.

Herein, we developed a self-supporting graphene (SSG) as a catalyst support via electrochemical intercalation for a flexible graphite sheet (FGS) in 1 M KOH aqueous solution. Then, we deposited $Co(OH)_2$ particles on FGS-SSG by a rapid microwave-polyol method. Fig. 1 displays the schematic for the preparation of $Co(OH)_2$/SSG-FGS. The in-situ growth SSG directly connected with the unexpanded FGS in which the unexpanded FGS acted as the current collector and the SSG served as conducting channels for fast electron transfer [27]. Meanwhile the self-supporting structure of FGS-SSG could avoid the aggregation effect of graphene layers and the use of extra binders, which were benefit for improving the OER catalytic activity of $Co(OH)_2$/SSG-FGS. Hence, the obtained $Co(OH)_2$/SSG-FGS composite electrode exhibited outstanding catalytic ability for OER and excellent durability in alkaline solution, even surpassed the commercial RuO_2 catalyst. This provided a new insight to prepare the composite catalyst of graphene and nanoparticles.

2. Experimental

2.1. Preparation of Co(OH)₂/SSG-FGS electrode

FGS-SSG which was derived from FGS was prepared firstly by electrochemical intercalation in 1 M KOH solution. Before used, all FGSs (1 cm × 3 cm × 0.2 mm) were successively cleaned with absolute ethyl alcohol and deionized water, vacuum dried at 60 °C for 24 h in an oven. After that, a couple of clean FGSs were connected to a potentiostat and immersed parallelly into 1 M KOH solution with their aligned area in the liquid of 1 cm². And the remaining part of FGS was encapsulated with the insulating material. Afterwards, the electrochemical intercalation for FGS was implemented in an 8 V cm^{-1} electric field for 5 min. At last, the cathodic FGS was rinsed gently with deionized water and vacuum dried at 60 °C for 24 h in an oven to obtain FGS-SSG.

$Co(OH)_2$/SSG-FGS composite electrode was prepared by the microwave-polyol method. First, homogeneous mixed solution of 0.05 M $Co(CH_3COO)_2$ containing ethylene glycol (EG) and water (H_2O) with the volume ratio of H_2O/EG = 0.08 was prepared with a sonication for 30 min. Next, immersed the as-prepared FGS-SSG into the mixture with a subsequent heating treatment for 30 s in a household microwave oven (Galanz, 2450 MHz, 800 W), then removed into cold water to cool quickly to ambient temperature.
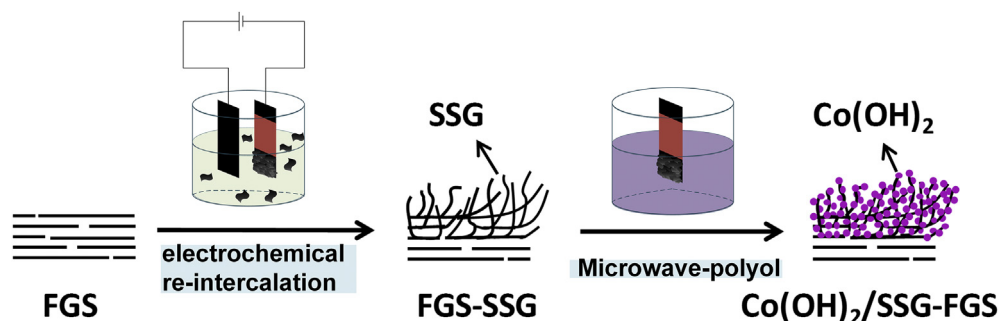

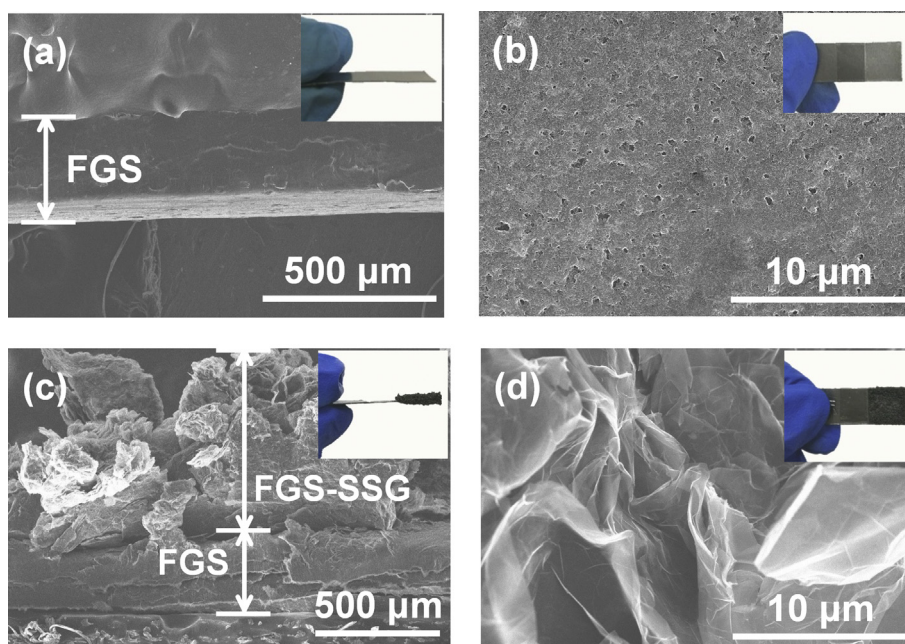**Fig. 1.** Schematic for the preparation of $Co(OH)_2$/SSG-FGS.

Fig. 2. SEM images of (a) FGS (side), (b) FGS (front), (c) FGS-SSG (side) and (d) FGS-SSG (front) (the insets showing the corresponding digital photographs).